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PROBLEMS OF TREATING WATER CONTAINING A ROTENONE PREPARATION (CHEM FISH REGULAR, AN EMULSIFIED ROTENONE PREPARATION) USED IN FISHERY MANAGEMENT

Robert A. Taft Sanitary Engineering Center
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PROBLEMS OF TREATING WATER CONTAINING A ROTENONE PREPARATION* USED IN FISHERY MANAGEMENT

*CHEM FISH REGULAR
AN EMULSIFIED ROTENONE PREPARATION

by

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U. S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
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The effects of an emulsified rotenone preparation (Chem Fish Regular) on water treatment and water quality were investigated. Use of this material is planned for fish eradication in the Dickinson Reservoir, the sole source of water for Dickinson, North Dakota. Experiments indicate that rotenone can be removed or detoxified and odor problems controlled by using active carbon. Odor due to decomposed fish can be controlled with moderate chlorine dosages. The effects of the rotenone treatment should be naturally dissipated within a few weeks. It appears feasible to produce a potable water from one treated with such a rotenone preparation. The worst difficulties are attributable to the hydrocarbon solvents used in the preparation.

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ABSTRACT

An investigation was made of the effects of an emulsified rotenone preparation (Chem Fish Regular) on water treatment and water quality. Use of this material in a concentration of 2 p.p.m. is planned for fish eradication in the Dickinson Reservoir which is the sole source of water for Dickinson, North Dakota.

Laboratory experiments indicated that the rotenone can be removed or detoxified and the odor problems due to the solvents and emulsifying agents can be controlled most effectively by the use of active carbon. Carbon dosages as high as 35 p.p.m. were required in these experiments to remove the odor while smaller amounts apparently removed the rotenone. A fish bio-assay technique was used to analyze for rotenone due to the lack of a suitable sensitive chemical analytical technique. The odor due to decomposed fish can be controlled with moderate chlorine dosages. The effects of the rotenone treatment should be naturally dissipated within a few weeks.

It appears quite feasible to produce a potable water from one which has been treated with such a rotenone preparation. The worst difficulties are attributable to the hydrocarbon solvents used in the preparation.

CONTENTS

	Page No.
Introduction	1
Rotenone	4
Chemistry	5
Toxicity to Fish	6
Toxicity to Mammals	8
Batch Treatment Experiments	9
Materials	9
Methods of Analysis	10
Chlorine Demand	12
Effect of Chlorine on Toxicity to Fish	12
Effect of Chlorine on Odor	16
Effect of Carbon on Toxicity to Fish	16
Effect of Carbon on Odor	17
Stability of Rotenone Solutions	18
Continuous Flow Treatment Experiments	20
Effect of Decomposed Fish	24
Alum Coagulation	25
Carbon Treatment	27
Effect of Chlorine	27
Conclusions and Discussions	28
Recommendations	30
Acknowledgments	31
References	33

PROBLEMS OF TREATING WATER CONTAINING A ROTENONE PREPARATION* USED IN FISHERY MANAGEMENT

Introduction

The investigation described in this report resulted from a request received from the Division of Water Supply and Pollution Control of the State of North Dakota in August, 1956. Plans had been made to conduct a fish eradication operation on Dickinson Reservoir which is the sole source of raw water supply for the City of Dickinson, North Dakota. Advice was sought on the feasibility, problems, and control of such an operation.

In the past decade, use of chemicals for destroying undesirable fish populations has become an increasingly important tool in fishery management. While fish poisons have been used for many years by fishery workers, primarily for sampling fish populations, development of a new concept in the management of sport fisheries brought about a tremendous expansion in the development and use of suitable piscicides. This concept, that the productivity of a body of water was limited, and, by proper management, could be channeled into producing a large harvestable population of desirable game fish, has been widely demonstrated. At present, most states have management programs of this type; some on rather large water areas.

Briefly, management consists of complete eradication of existing fish populations, generally predaceous, nondesirable, nonharvestable or stunted,

*Chem Fish Regular - An emulsified rotenone preparation

populations, and of restocking with fry or fingerlings of a suitable species. These fish, freed from predation and competition for food, make rapid growth and provide a phenomenal increase in sport fishing.

In order to provide a suitable agent for destroying fish populations, much work has been done on the development of piscicides until today there are many commercial preparations on the market. Most of these incorporate rotenone, one of the most powerful fish poisons known, as the toxic principle.

The difficulty in handling and evenly applying derris or cube ground root, rotenone sources containing about five percent, in large water areas, led to the development of various formulations. Most of these incorporate rotenone and other root extractives, various solvents and wetting agents into liquid or paste formulations. Some may contain synergists, and others may incorporate different toxic ingredients. The cost, ease of application, safety, and effectiveness in destroying fish populations are the major considerations in fish management.

With increased use of water supply reservoirs for recreational purposes and possible use of these piscicides for fish management, a major consideration must be the effect on water quality and potability. Since no information on this subject was available, it was necessary to develop such data from laboratory and pilot plant investigations.

The chemical compound chosen for the project was Chem Fish Regular which is manufactured by Chemical Insecticide Corporation, 30 Whitman Ave.,

Metuchen, New Jersey. According to the manufacturer's specifications, this preparation contains the following ingredients:

Active Ingredients		70%
Methylated naphthalene	55.0%	
Other cube extractives	10.0%	
Rotenone	5.0%	
Inert Ingredients		30%

Information from the manufacturer indicates that the inert ingredients consist, at least in part, of 5 - 10% acetone, added to increase solubility of rotenone, and 15% of emulsifying agents of the nonionic and anionic types.

While the manufacturer's recommended dosage for this preparation is 0.5 to 1.0 p.p.m. of Chem Fish Regular for satisfactory fish eradication, we understand that the North Dakota Fish and Game Department intends to use 2.0 p.p.m. in the Dickinson operation in order to insure a complete fish kill.

Use of this preparation in public water supply requires consideration of the following effects:

1. Toxicity of rotenone to humans, other mammals, and to fish in household aquaria.
2. Effect of Chem Fish Regular components on water treatment processes and conversely the effect of treatment on the Chem Fish Regular components.

3. Taste and odors produced by the solvent and emulsifying agents.

4. Tastes and odors which may result from decomposing fish and other aquatic life.

The investigation of Chem Fish Regular compound in the raw water supply was based on the fair assumption that essentially all of the compound's components would have to be removed or chemically altered to produce a finished water of acceptable quality. It was presumed that of the several ingredients of Chem Fish Regular, two would be likely to cause difficulty: (1) rotenone and the related cube extractives, and (2) the hydrocarbon solvent, methylated naphthalene. Accordingly, the following investigations were made on the rotenone compounds and solvent components of Chem Fish Regular.

1. Removal by alum coagulation.

2. Removal by lime softening.

3. Effect of Chlorine.

4. Effect of Carbon treatment.

The investigation can be divided into two parts: (1) laboratory work using bench scale quantities and equipment, and (2) continuous flow in a small model water treatment plant.

Rotenone

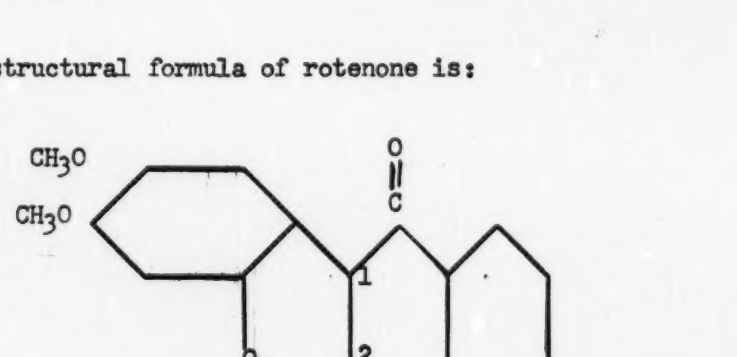
As indicated previously, Chem Fish Regular contains both rotenone and cube extractives. A brief review of the chemistry of these compounds

will enable a better evaluation of the hazard they may pose in drinking water and of the effectiveness of their removal or detoxification by standard water treatment practices.

Chemistry

Rotenone is a colorless, odorless, crystalline constituent of certain tropical leguminous plants. The principal sources are from the plant genera Derris and Lonchocarpus or cube root. Rotenone is extracted from the finely ground plant material with such solvents as ether or chloroform. In addition to rotenone, cube root extraction yields certain other constituents, such as deguelin and elliptone and the derivatives, sumatrol, toxicarol and malaccol which are the hydroxy compounds respectively of rotenone, deguelin, and elliptone. Other derivatives are readily formed spontaneously by the action of light and air. Most of these compounds have less toxicity than rotenone itself; some practically no activity at all.

The structural formula of rotenone is:



Oxidation of rotenone either by the action of light and air or by oxidizing agents such as permanganate or chlorine results in the removal of two H atoms from the 1 and 2 position to produce a double bond compound called dehydrorotenone. Further oxidation results in the splitting of the molecule. These oxidation compounds are relatively inert products physiologically.

Rotenone is extremely soluble in chloroform and to a lesser extent in many other organic solvents. In kerosene the solubility is less than 1-2000. It is practically insoluble in water, the values given in the literature range from 1-6,000,000 to 1-1,000,000. The very low solubility of rotenone and extractives in water is not, however, a deterrent to their use in water as a fish poison, due to the extreme susceptibility of fish to the action of rotenone. As little as 0.075 mg/l of rotenone at 27° C kills goldfish in 2 hours. An interesting comparison is that, to goldfish, rotenone is twenty-five times as toxic as potassium cyanide.

Toxicity to Fish

The extreme toxicity of rotenone to fish is well documented (1, 2, 3, 4, 5, 6). Under controlled laboratory conditions, values as low as 0.05 p.p.m. of formulations containing five percent rotenone have been found toxic to very sensitive fish, such as trout, while 0.5 p.p.m. have not given a complete kill of less sensitive species, such as the brown bullhead. Other species appear to be susceptible somewhere between these values. Field studies, however, have been reported in which complete kills were not obtained from applications

exceeding 1 p.p.m. and in a few cases even 2 p.p.m., possibly due to the difficulties involved in obtaining uniform dispersal. Fisheries' workers generally consider 2 p.p.m. of formulations containing five percent rotenone necessary to insure a complete kill.

Toxicity to fish following application of rotenone has been reported in various investigations to persist for from one to thirty days, depending on conditions. Among water conditions which may affect toxicity and persistence of rotenone are temperature, pH, alkalinity, turbidity, the presence of a thermocline and depth.

Toxicity of rotenone, and rate of dissipation increase with increasing water temperatures. In waters with normal summer temperatures (60 to 80°F) toxicity has largely dissipated within a week but in winter may persist longer.

There is apparently little difference in the quantity of rotenone necessary to effect a fish kill in acid and alkaline waters. Persistence, however, is somewhat longer in acid waters. Rotenone also persists longer in turbid than in clear waters.

Presence of a thermocline may effectively prohibit passage of rotenone to deeper water. Even in the absence of thermal stratification, rotenone formulations do not satisfactorily penetrate depths of over 30 feet unless the material is mechanically introduced into the deeper waters.

The lethal action of rotenone has been largely attributed to constriction of the gill capillaries preventing passage of blood through the gills, thus shutting off the oxygen supply.

Various fish food organisms, such as insect larvae and mollusks, have been reported as somewhat less susceptible to the toxic action of rotenone than fish. Some zooplankton organisms, especially microcrustaceans are affected but phytoplanton and other aquatic vegatation are apparently unaffected in concentrations that kill fish.

Toxicity to Mammals

The acute toxicity of rotenone by the oral route is unusual in that it is marked by a wide variation among species (9) varying from approximately 60 mg/kg for the guinea pig, 130 mg/kg for the albino rat, approximately 1.5 g/kg in rabbits, to approximately 3 g/kg in dogs (7). The effects from acute single oral doses consist of severe irritation of the gastrointestinal tract; in dogs, cats, and pigeons emesis accompanies a toxic dose. On an acute oral basis rotenone would be classed according to a conventional system as bordering on the "highly toxic" for the guinea pig but only "slightly toxic" for the rabbit and dog.

Rotenone is far more acutely toxic by other routes of administration either intraperitoneally or intravenously, 2 mg/kg being the acude LD_{50} for the guinea pig intraperitoneally, and 0.65 mg/kg for the dog and cat intravenously when the rotenone was administered in ethylene glycol; on the basis of dose administered, ethylene glycol was considered to be noninjurious in control animals (9).

Chronically administered during a two-year period in the diet of rats, rotenone produces necrosis in the liver at a level of only 5 parts per million (8); the same degree of tissue damage would require about 2 times the dose of mercuric acetate, a well-recognized cellular poison. On a diet of 150 milligrams rotenone/kg of food, fetuses of pregnant guinea pigs either failed to survive until birth, or died shortly thereafter (9).

Because no reports exist of man being poisoned by rotenone, it is assumed that man is one of the more highly resistant species. The fact that man has eaten fish killed by rotenone unfortunately provides no evidence on this point because the peculiar injury of rotenone to the gills of fish makes it doubtful that any significant amount would enter the fleshy part of the fish that is eaten. The fact that rotenone has been used as a spray on edible foods likewise provides no evidence of its lack of toxicity for man because its instability in air and sunlight causes the destruction of a major portion of the residue on such foods before they are eaten.

No reports have come to our attention of the relative toxicity of rotenone to swine and ruminants.

Batch Treatment Experiments

Materials

The rotenone preparation used in the experimental work was Chem Fish Regular, the composition of which was described elsewhere in this report. Two different waters were used: one, a clear, hard, highly

mineralized water, which is designated Hatchery water; the other, Ohio River water, which is moderately hard and contains some turbidity. Some characteristics of these waters are shown in Table 1:

Table 1

Water Characteristics	Hatchery Water	Ohio River Water
pH	7.7 - 8.0	7.5
Alkalinity, mg/l	280 - 310	39
Hardness, mg/l	380	206
Turbidity, units	<5	30

The activated carbon used in all of the experimental work was Aqua Nuchar A, a grade of carbon widely used in water treatment.

Methods of Analysis

Initial attempts to use a chemical method for quantitative determination of rotenone compounds in water proved unsuccessful with the low concentrations involved. Bio-assays with fish were used to determine the loss in toxicity and to estimate the amount of Chem Fish Regular remaining after the various treatments. All other chemical and physical determinations were made according to Standard Methods, 10th Edition (10).

Many investigators have used bio-assays with organisms, such as mosquito larvae and houseflies, to estimate insecticide residuals in water and foods. Bio-assay methods to determine toxicity of chemicals to fish have been reasonably well established (Doudoroff et al). (1) In previous studies in this laboratory, bio-assays with fish were used to estimate quantities of dieldrin in runoff from areas on which the

insecticide had been applied. The data indicated that quantities of dieldrin could be estimated within 25 percent of the actual concentration. As fish are extremely sensitive to rotenone, it was believed that this method could be used to estimate quantities of Chem Fish Regular remaining after various treatments. The method consisted, briefly, of establishing a standard curve relating concentration of chemical to the time of loss of equilibrium or death of fish. By introducing fish into unknown concentrations under the same test conditions and referring to this curve, quantities could be estimated.

In this study, standard curves were prepared as follows: a logarithmic series of concentrations (e.g. - 0.1, 0.18, 0.32, 0.56, 1.00 etc. p.p.m.) of Chem Fish Regular in the test water was prepared. Five fathead minnows (Pimephales promelas) of a fairly uniform size - 2-2½ inches long and weighing from 1 to 1½ grams - were added to duplicate 10 liter quantities of each concentration in five gallon, wide-mouth, glass bottles. The temperature was maintained at 22° C. Observations were made as to the time necessary for loss of equilibrium and death of each fish.

From observations made on replicate experiments, it was found that time for loss of equilibrium of 50 percent of the test fish was the most satisfactory criterion to use as an end point in these experiments. A wider range of concentrations could be determined, shorter time periods were involved, and less variation in the susceptibility of individual fish was apparent than for death times. Extreme care was exercised in

conducting these experiments as variables, such as temperature, water quality, acclimatization of fish, and the age of test solutions may have a considerable effect on the time of fish reaction.

The 50 percent loss of equilibrium time was plotted against concentration on a log-log scale to obtain a standard curve. Typical standard curves obtained under different experimental conditions are shown in Figure 1.

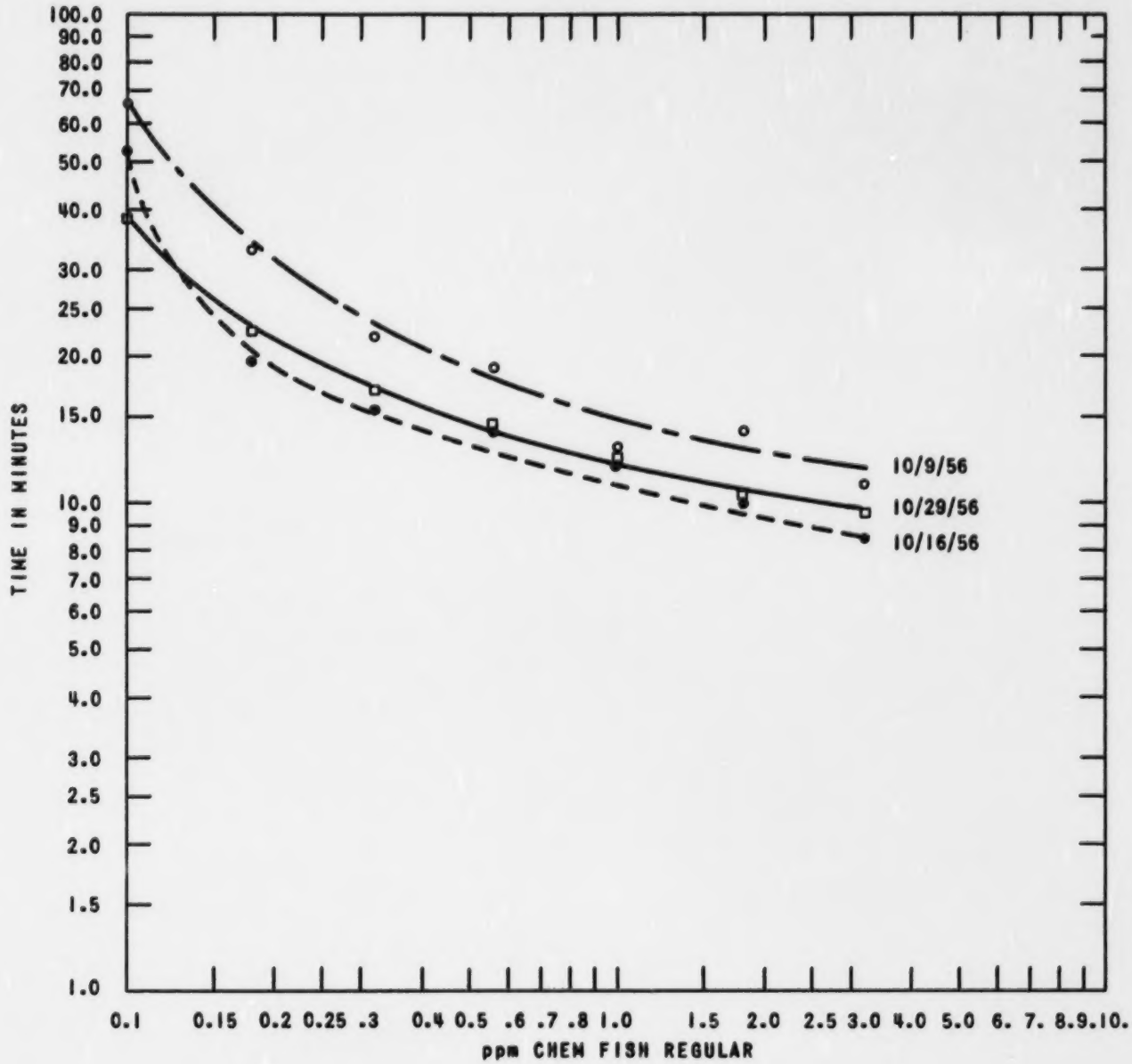
Concentrations of Chem Fish Regular were estimated by adding five fish to 10 liters of treated effluents, determining 50% loss of balance time and referring to the standard curve. With the test fish used, the minimum concentration of Chem Fish Regular that could be estimated was 0.1 p.p.m.

Chlorine Demand

A chlorine demand determination was made on a 2 p.p.m. solution of Chem Fish Regular in ammonia free water. Contact time was 30 minutes at a temperature of 24° C. Up to 15 p.p.m. of chlorine were added to the 2 p.p.m. Chem Fish Regular solution without showing an appreciable chlorine consumption. From these results, it can be expected that the components of Chem Fish Regular will not exert a significant demand on the chlorine application in the water treatment plant.

Effect of Chlorine on Toxicity to Fish

Many investigators working with rotenone have observed that the compound is easily oxidized when exposed to air and light.(2) The compound is also readily oxidized by potassium permanganate. Lawrence (11)



STANDARD LOSS OF BALANCE CURVES ON 3 DIFFERENT DAYS IN HATCHERY WATER. TEMP. 22° C

Figure 1

demonstrated that 2.0 p.p.m. of potassium permanganate could detoxify 1.0 p.p.m. of Nox Fish, which was equivalent to .05 p.p.m. of rotenone. Oxidation with permanganate was rapid. Fish survived in water to which rotenone and potassium permanganate were added at the same time. It was expected that chlorine would be equally as effective.

Varying amounts of chlorine were added to Hatchery water containing 2 p.p.m. of Chem Fish Regular and allowed to stand at room temperature of about 24° C. At the end of varying times of contact, sufficient sodium thiosulfate was added for dechlorination purposes, and the water was then subjected to fish assay to determine the quantity of Chem Fish Regular remaining. Appropriate controls were also set up. These data are shown in Table 2. The effectiveness of chlorine as a detoxification agent is dependent upon the dose applied and time of contact. With a hard water such as Hatchery water, the minimum amount of chlorine for detoxification with a contact time of three hours is 9.5 p.p.m. Twenty-five p.p.m. chlorine are required, however, when the contact time is reduced to 30 minutes.

Potassium permanganate oxidation of Chem Fish Regular solution was not tried since it is not a common chemical in water treatment. While chlorine does detoxify Chem Fish Regular solutions, it appears that it is not as effective an agent as potassium permanganate, since greater amounts of chlorine and longer contact times were required for detoxification.

Table 2

Effect of chlorine and contact time on Chem Fish Regular in hatchery water

p.p.m. chlorine added	Contact time-minutes				
	15	30	60	120	180
	p.p.m. Chem Fish Regular remaining				
2.4	2.0	2.0	1.7	1.5	0.9
4.5	>2.0	---	>2.0	>2.0	.65
4.8	2.0	2.0	2.0	1.5	.48
9.1	1.3	1.1	.65	.36	.11
9.5	1.0	.75	.56	.19	<.1
13.6	1.1	.85	.17	<.1	<.1
15.0	1.6	.70	.20	<.1	<.1
20	1.6	1.1	.18	<.1	<.1
20	.52	.16	<.1	<.1	<.1
25	.23	.11	<.1	<.1	<.1
25	.36	<.1	<.1	<.1	<.1
30	.22	<.1	<.1	<.1	<.1

Effect of Chlorine on Odor

The odor of Chem Fish Regular in water is due almost exclusively to the solvent, methylated naphthalene. This hydrocarbon would not be expected to be affected by chlorine. To check this assumption experimentally and to make sure that odor was not intensified by chlorine, a few tests were made. These data are shown in Table 3.

Table 3

Effect of chlorine on odor due to 2 p.p.m. Chem Fish Regular

p.p.m. chlorine added	Time of contact-minutes		
	15	120	180
	Threshold odor remaining		
0	64	--	--
20	32	16	16
25	16	16	16
30	--	16	16

Some reduction in odor was, in fact, obtained although in practice it would be an ineffective method to use.

Effect of Carbon on Toxicity to Fish

Varying amounts of active carbon were added to Hatchery and Ohio River waters containing 2 p.p.m. Chem Fish Regular. The suspension was stirred to maintain adequate contact for 30 minutes and then filtered

through one foot of fine sand in a column to remove the carbon. Concentrations of Chem Fish Regular remaining were determined by fish bio-assay. Suitable controls showed that sand filtration removed no toxic components. These data are shown in Table 4.

Table 4

Effect of carbon on Chem Fish Regular toxicity

p.p.m. carbon added	p.p.m. Chem Fish Regular remaining		
	Hatchery water	Ohio River water	
5	2.0	1.5	--
10	1.0	1.2	--
15	.7	--	.7
20	.15	.7	<.1
25	<.1	--	<.1
30	<.1	<.1	<.1

The results indicate that 25 p.p.m. of carbon will remove the toxicity of 2 p.p.m. Chem Fish Regular from both Hatchery and Ohio River waters.

Effect of Carbon on Odor

The effectiveness of the removal of odor by activated carbon was determined in the same way as for toxicity removal, with the following results shown in Table 5.

Table 5

Effect of carbon on Chem Fish Regular odor

p.p.m. carbon added	Threshold odor remaining	
	Hatchery water	Ohio River water
0	64	64
5	32	--
10	16	--
15	4	2
20	0	1
25	0	1
30	0	0

Complete removal of odor from Hatchery water would require addition of 20 p.p.m. of carbon. Lesser amounts of carbon, 15 p.p.m., yield an effluent with an odor threshold of 4. Waters, not uncommonly, may contain threshold odors of this magnitude and be quite acceptable to the consumer. In this instance, however, it is believed that the hydrocarbon odor would be sufficiently repugnant to most consumers that complete removal would be necessary.

Stability of Rotenone Solutions

Reports in the literature had shown that aqueous rotenone solutions decompose upon standing due to the action of light and air. Reported time for decomposition varied considerably in the literature. Two experiments were performed to check reduction of toxicity and odor on standing.

Two p.p.m. of Chem Fish Regular were added to 100 liters of Hatchery water contained in a stainless steel tank from which light was excluded by a cover. Samples were withdrawn from a tap at the bottom of the tank after some agitation to obtain a representative portion for analysis. Results obtained are tabulated in Table 6.

Table 6

Stability of 2.0 p.p.m. Chem Fish Regular in Hatchery water

	Time Days	Temp. °C.	p.p.m. ChemFishReg Remaining	Odor Remaining
Experiment #1	0	12	2.0	64
	1	12	2.0	64
	2	14	2.0	64
	3	16	1.7	64
	8	16	<.1	2
Experiment #2	0	19	2.0	32
	1	20	1.2	8
	2	20	<.1	2
	3	21	<.1	0

It is readily apparent from these data that Chem Fish Regular solutions are not stable. Rate of decomposition is dependent upon temperature. With low temperatures, 12-16°C., the solution was stable for at least three days. At higher temperatures, 19-21°C., residual p.p.m. Chem Fish Regular and threshold odor were <.1 and 0 at the end of three days.

Continuous Flow Treatment Experiments

Laboratory experimentation involving batch treatment of Chem Fish Regular solutions was supplemented by a continuous flow model water treatment plant. A typical experimental run, along with a brief description of the physical plant, is as follows.

Chem Fish Regular, at a concentration of 2 p.p.m. in Hatchery water, was thoroughly mixed in a stainless steel contaminant tank in sufficient volume for an eight-hour run. The contaminated water was pumped to a rapid mix chamber at the rate of about 330 ml per minute. Treatment chemicals were pumped to the rapid mix chamber from individually stirred solution bottles. Chemical doses were controlled by means of metering pumps.

The treated water flowed by gravity to a small plastic flocculating tank, equipped with revolving paddles to maintain adequate flocculation. The capacity of this tank, about 10 liters, yields a theoretical detention time of about 30 minutes. From the flocculating tank the flow entered a plastic sedimentation tank with a calculated detention time of 8-12 minutes. Supernatant overflowed a weir to a distribution box which split the flow to two identical sand filters.

The filters consisted of 30 inches of sand on 15 inches of graded gravel, all contained in a plastic column two inches in diameter. The design rate for these filters is two gallons per square foot per minute. Samples for fish bio-assay, odor removal, and chemical analyses were obtained from the filter effluent.

In these experiments, Hatchery water contaminated with 2.0 p.p.m. of Chem Fish Regular was treated with alum, lime, and varying doses of carbon to determine the combination which would yield a safe and potable water. The latter criteria were established by fish bioassay and odor determination on the plant effluents. The doses of alum and lime used in this series of experiments were experimentally determined to yield a good coagulation and maximum softening on the test waters. A summary of the data obtained are presented in Tables 7 and 8.

Chemical treatment of Hatchery water containing 2 p.p.m. of Chem Fish Regular compound with alum and lime does not remove the toxic materials nor does it significantly reduce odor due to the hydrocarbon solvent. The two low values in Table 7 obtained on Chem Fish Regular remaining after chemical treatment demonstrate that rotenoid compounds are not stable but are readily decomposed upon standing. It is apparent from Table 7 that supplemental treatment, in addition to alum and lime, is needed to produce potable water.

Table 8 is a summary of the data obtained when varying carbon doses were used in addition to alum-lime softening. Moderate doses of carbon are required to reduce the Chem Fish Regular concentration to non-toxic quantities. Fifteen p.p.m. carbon yields a water which will not adversely affect fish. To obtain an odor-free effluent, larger doses of carbon, 33-35 p.p.m., are necessary.

Table 7

Effect of coagulation and softening on 2 p.p.m. Chem Fish Regular solution

Sample data			Chemical dose		Water quality		Chemical analyses				
Sample No.	Sample	Temp. °C.	p.p.m. alum	p.p.m. lime	Chem Fish Regular remaining	Threshold odor	Hardness as $CaCo_3$	Calcium as $CaCo_3$	Total alka-linity	Phenol. alka-linity	pH
1	Inf.	20	--	---	2.0	64	384	238	307	0	7.7
2	Eff.	20	50	505	2.0	8	114	72	24	8.7	9.6
3	Eff.	20	44	458	2.0	8	118	55	29	10	9.6
4	Eff.	14	38	436	—	32	134	94	53	42	10.9
5		14	37	448		64	117	69	33	23	10.5
6	Eff.	16.5	42	467	—	32	122	76	37	29	10.6
7	Eff.	16.5	42	501	0.4*	32	122	85	36	28	10.6
8	Eff.	18	28	465	0.5*	32	110	58	31	18	10.1
9	Eff.	16	42	423	--	32	117	75	31	23	10.5

* Samples allowed to stand over weekend before assayed. Values known to be low.

Table 8

Carbon treatment of 2 p.p.m. Chem Fish Regular Solution

Sample data			Chemical dose			Water quality		Chemical analyses				
Sample No.	Sample	Temp. °C.	p.p.m. alum	p.p.m. lime	p.p.m. carbon	Chem Fish Regular remaining	Threshold odor	Hardness as $CaCo_3$	Calcium as $CaCo_3$	Total alkalinity	Phenol. alkalinity	pH
1	Inf.	21.5	--	---	--	2.0	64	384	238	307	0	7.7
2	Eff.	21.5	45	440	8	0.4	8	134	40	38	8.5	9.4
3	Eff.	21.5	56	497	10	0.2	1	153	104	61	51	10.8
4	Eff.	19.5	48	470	15	<.1	2	154	106	61	51	10.7
5	Eff.	19.5	46	445	15	<.1	4	135	90	44	36	10.6
6	Eff.	18	41	423	25	<.1	4	117	61	26	12	9.8
7	Eff.	19	40	423	23	<.1	4	134	57	47	6.4	9.3
8	Eff.	20.5	22	425	31	<.1	2	151	58	57	6.6	9.1
9	Eff.	20.5	41	455	31	<.1	2	137	51	48	7.9	9.3
10	Eff.	20.5	42	470	33	<.1	0	116	55	29	11	9.7
11	Eff.	20.5	43	467	35	<.1	0	116	59	25	9.6	9.7

No attempt was made to determine what doses would be necessary when the combination of chlorine and carbon was used. Some reduction of odor was obtained with 20 p.p.m. chlorine, although complete removal was obtained only with carbon. It is believed that disinfection quantities of chlorine will not greatly reduce the amount of carbon required to remove all of the odor.

Effect of Decomposed Fish

Hoffman and Payette (12), in their report on fish eradication operation in Hodges Reservoir, show that all fish killed by rotenone do not come to the surface immediately where they may be harvested. In fact, as long as 11 - 13 days after rotenone application, 64.2 tons of fish had been released from the lake bottom and were recovered from the lake surface. This sort of delayed dead fish appearance has also been reported in other operations.

Since dead fish probably will remain in the lake long enough for decomposition to occur, and since the odor of dead fish would be objectionable to consumers, experiments were undertaken to determine the effectiveness of coagulation, chlorination, and carbon treatment in removing the odor.

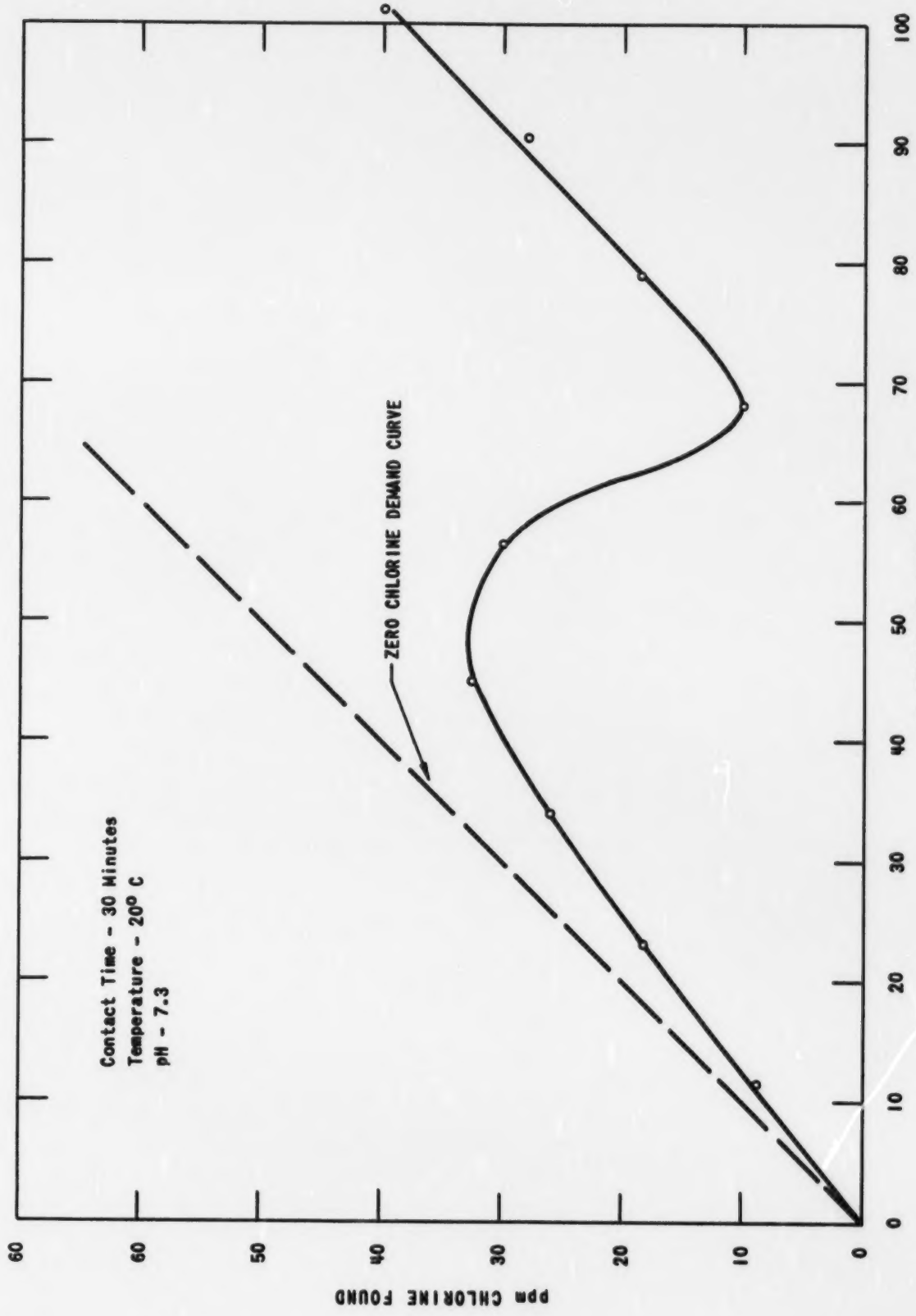
Since there was no way of estimating the amount of odor which would be encountered, an arbitrary quantity was used which would at least demonstrate the characteristics of the water and the method for removal of the odor. Twenty fish, weighing 24 grams, which had been

killed by rotenone were put into 20 liters of Hatchery water and allowed to stand for two days at room temperature of 21° C. The decomposed fish were removed, and the odorous water was then stored in the refrigerator at 1 - 2° C.

A quantitative measurement of the odorous water was obtained by the standard threshold odor determination and a 30-minute chlorine demand. The threshold odor was found to be 2048. Figure 2 reveals that a classical type of chlorine demand curve is obtained. This probably reflects the presence of ammonia or amines which are always associated with decomposing fish. The 30-minute demand was 68 p.p.m. of chlorine.

Alum Coagulation

Resistance of odor and chlorine demand compounds to alum coagulation was determined by coagulating Hatchery water containing 10% by volume of odorous water with varying amounts of alum from 40-90 p.p.m. Both odor and chlorine demand determinations were performed on the effluents. Water which had been treated with 90 p.p.m. of alum gave an effluent with a threshold odor number of 128 and a chlorine demand of 6.5. This corresponds fairly closely to a 1-10 dilution of the odorous water, which would give 205 and 6.8 for threshold odor number and chlorine demand, respectively. Alum coagulation alone has no significant effect on either odor or chlorine demand and will not produce a potable effluent.



CHLORINE DEMAND OF ODOROUS WATER

Figure 2

Carbon Treatment

Odor removal by active carbon was checked by adding increasing amounts of carbon to a 5% by volume solution of odorous water in Hatchery water. As in previous tests, threshold odor number and chlorine demand determinations were made on the effluents. The odor was completely removed by 40 p.p.m. of carbon. A threshold odor number of two was obtained with 30 p.p.m. of carbon. The chlorine demand of the effluents was not significantly reduced. This would indicate that the odor of the decomposed fish was due to protein decomposition products other than amines and ammonia. These latter compounds apparently resist carbon adsorption, and would exert a chlorine demand.

Effect of Chlorine

A further test was made on the effect of varying doses of chlorine on the odor. The intention was to rule out the possibility of odor intensification. Amounts of chlorine ranging from 0.9 to 4.6 p.p.m. were added to a 5% solution of odorous water in Hatchery water. Simple dilution of the odorous water to 5% would yield a threshold odor number of 10 and a chlorine demand of 3.4 p.p.m. The following results show that chlorine does not intensify the odor, rather it destroys it when free residual chlorine is obtained.

Table 9

Effect of chlorine on decomposed fish odor in water

p.p.m. chlorine added	0.9	1.8	4.6
Threshold odor no.	4	1	0

Conclusions and Discussions

The proposed treatment of Dickinson Reservoir with 2.0 p.p.m. of Chem Fish Regular, while withdrawing water for treatment and distribution to the city of Dickinson, appears to be entirely feasible. Although rotenone is a relatively toxic material and its routine use in water supplies would be looked upon with disfavor, its infrequent use for fish management should present no hazard if adequate measures are taken for its removal by treatment or until it has been destroyed by natural processes. To remove the rotenone and odorous substances, especially the solvents present in Chem Fish Regular will require relatively large doses of chemicals.

The chemical dosages required to produce good quality of water in this investigation are summarized in Table 10.

Table 10

Summary of data on treatment of water containing Chem Fish Regular

Conditions	Chlorine - p.p.m.		Carbon - p.p.m.	
	Odor	Toxicity	Odor	Toxicity
Batch	Some reduction with 30 p.p.m.	9.5 p.p.m. 3 hrs. contact 25 p.p.m. 30 min. contact	20	25
Continuous flow	--	--	35	15

Both chlorine and carbon can effectively remove toxicity due to rotenone. Odor, however, is removed completely only by carbon. Carbon treatment in the indicated dose, then, is clearly the method to use to produce a potable water.

Since the application of Chem Fish Regular is a "one shot" occurrence, the increased chemicals cost should not be prohibitive. The critical period at the water plant should be relatively short. For rotenone toxicity, this time should not be more than a week in view of the instability of this compound. Odor problems may persist longer, perhaps for a month, but with decreasing intensity during that period. The odor problem due to the decomposition of the killed fish can be effectively controlled with moderate chlorine doses.

The actual amount of carbon that may be necessary in practice may vary from the doses determined in this report for at least these reasons.

1. Difference between the test waters and the water in Dickinson Reservoir.
2. Expected variation in the sensitivity of consumers to hydrocarbon tastes and odors in drinking water.
3. Possible variations in the concentration of Chem Fish Regular in the water plant influent. While an average of 2 p.p.m. may be applied, portions of the reservoir will receive greater amounts.
4. In this report <.1 p.p.m. of Chem Fish Regular was considered nontoxic. Household aquaria may contain tropical fish which are more sensitive to rotenone than the bioassay fish used.
5. A safety factor may be advisable. In practice it probably would be wise to add 50 p.p.m. carbon instead of the 35 p.p.m. found necessary in the continuous flow experiments.

Recommendations

While use of Chem Fish Regular would present no impossible problems to the water plant, there is, however, some objection to use of this preparation or any formulation using this hydrocarbon solvent. The hydrocarbon odor persists for a relatively long period of time compared to the rotenone, and is also more difficult to remove.

Complete removal of the hydrocarbon is necessary since the odor is quite repugnant to most people. It would seem that a preparation which does not use this hydrocarbon solvent would present fewer problems for the water treatment plant. The manufacturer of Chem Fish Regular indicates that a hydrocarbon of lower boiling range and containing less odorous components may be used for the formulation. This hydrocarbon solvent is now being checked in this laboratory and a supplementary report on the data obtained will be written at some later date. If the Dickinson plant is not now equipped to feed as much as 50 p.p.m. of carbon, temporary facilities to permit these doses should be provided and carbon stocks obtained sufficient to provide 20 p.p.m. of carbon for one month.

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